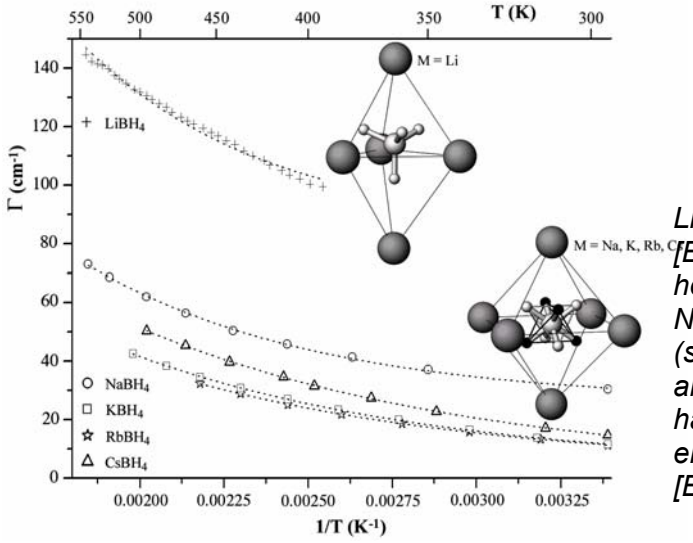
## Project H-8: Destabilization of metal hydride complexes and theoretical modeling

**K. Yvon** *IEA HIA 2003 AR*
**University of Geneva, Geneva, SWITZERLAND**
*E-mail: klaus.yvon@cryst.unige.ch*

The reorientation motions of the $[BH_4]^-$ anions in the series $MBH_4$ (M=Li, Na, K, Rb, Cs) have been measured by neutron diffraction and Raman spectroscopy in the absence of catalysts. For the cubic modifications of M=Na, K, Rb and Cs, the analysis of the line widths suggests that the energy barrier of reorientation of the $[BH_4]^-$ anions decreases as a function of cation size in the sequence Na: 12.1(5), K: 9.2(4), Rb: 8.8(3) and Cs: 8.2 (4) kJ/mol (see Figure below). For the hexagonal modification of $LiBH_4$ the data suggest two energy barriers of reorientation at ~5 and ~60 kJ/mol, respectively. These results show that the compounds undergo a significant softening of their structure also in the absence of catalysts while the integrity of their tetrahedral $[BH_4]^-$ complexes is maintained. The data also show that substituting lithium by heavier alkali metals has a destabilizing effect. Similar experiments were also performed at low temperature. The results show that there exists a linear relation between B-D bond lengths and the Raman shifts of the totally symmetric stretching mode, $\nu_1$, and confirm that a general softening of the tetrahedral $[BH_4]^-$ complexes occurs in the presence of heavier (larger) alkalines.

On the other hand, various alanate samples of composition $NaAlH_4$ have been examined in collaboration with C. Jensen (Univ. of Hawaii) in view of their destabilization by doping and ball milling. This compound is presently used as a hydrogen storage medium for PEM fuel cells in pilot projects for the transportation sector. The aim of our work was to investigate the reasons for the beneficial influence of doping on the kinetics. For this purpose doped and milled samples have been investigated separately. This was done because in practice doping is performed by mechanical milling, i.e. the relative influence of these two effects on hydrogen desorption properties is unknown. The interpretations of our Raman, IR and diffraction data are under way.




*Line width, $\Gamma$, (in $cm^{-1}$) of the $\nu_2$ band of $[BH_4]^-$ as a function of temperature in hexagonal $LiBH_4$ (crosses) and cubic $NaBH_4$ (circles), $KBH_4$ (square), $RbBH_4$ (stars) and $CsBH_4$ (triangles). Dotted lines are fits of the experimental data to a model having one energy barrier. Inserts show environments of the (disordered) tetrahedral $[BH_4]^-$ anions in the alkaline metal cavities.*